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# **BEST TECHNICAL APPROACH FOR THE PETROLEUM QUALITY ANALYSIS (PQA) SYSTEM**

**INTERIM REPORT  
BFLRF No. 300**

By

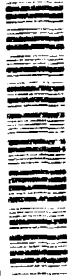
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## EXECUTIVE SUMMARY

**Problems:** Recent U.S. military operations have identified a need for improved methods of fuel and lubricant analysis in the field. This analysis capability should be highly mobile and built around modern, state-of-the-art analytical techniques.

**Objective:** The objective of this project was to develop a best technical approach to meet the U.S. Army's future requirements for portable fuel and lubricant analysis.

**Importance of Project:** Through implementing the recommendations presented in this report, the frequency and severity of fuels-related equipment failures may be minimized, thus increasing the useful life of the affected machinery at a minimum cost.

**Technical Approach:** Current U.S. Army fuel and lubricant testing requirements and capabilities were examined and evaluated. These evaluations were followed by a critical review of future testing needs. Tests which should be included in a mobile testing capability were determined. Finally, a proposed best technical approach to meet future fuels testing requirements was developed.

**Accomplishments:** A trade-off analysis was performed on each of the tests required under MIL-HDBK-200G. Based on the results of the trade-off analysis, a testing protocol and methods to conduct the tests were developed.

**Military Impact:** The proposed Petroleum Quality Analysis (PQA) system would be capable of rapid, accurate, on-site evaluation of mobility fuels. Incorporation of the tests recommended in this report would result in a more efficient method of fuel and lubricant analysis in the field.

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## I. INTRODUCTION

Military operations in Grenada and Panama, and more recently, Operations Desert Shield and Desert Storm, all suffered from inadequate field capabilities to properly analyze fuels and lubricants. The means to perform timely analyses of fuels and lubricants is critical since the use of incorrect or contaminated fuel can result in problems ranging from plugged fuel filters to engine damage and loss of aircraft. During the operations in Grenada and Panama, and Operations Desert Shield and Desert Storm, it was often the case that any fuel sample that required laboratory analysis had to be sent out of the theater. This caused a delay of two to three days, or longer, before fuel was approved for use. Often the need for fuel superseded laboratory analysis and evaluation, and the fuel was consumed before fuel quality could be verified through analytical chemical laboratory data.

The Defense Fuel Supply Center (DFSC) is responsible for the purchase and delivery of all petroleum, oil, and lubricant (POL) products used by the Department of Defense. The DFSC maintains custody and assures the quality of all purchased POL products until the products are transferred to the customer, i.e., the U.S. Army. After the Army takes possession of any POL product, it also assumes responsibility for the quality of that product.

Mobility fuels (i.e., engine fuels) are purchased as bulk, unpackaged POL. Every effort is made to prevent contamination or mixing of different grades of fuel during delivery and storage. However, since any given batch of fuel may move through numerous fuel storage tanks, delivery trucks, and even vehicle fuel systems before it is ultimately burned in an engine, the task of maintaining fuel identity and quality is quite difficult.

Requirements and procedures that govern the storage, delivery, and custody transfer of Army-owned fuels and other POL products are detailed in Military Standardization Handbook, MIL-HDBK-200G, "Quality Surveillance Handbook for Fuels, Lubricants, and Related Products."<sup>(1)</sup>\* The testing requirements vary with the type and age of the product and the relative position in the distribution chain. A synopsis of these requirements is presented in this report.

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\* Underscored numbers in parentheses refer to the list of references at the end of this report.

To perform accurate and timely field analyses of POL products, the Army identified the need for a modern, state-of-the-art petroleum quality analysis capability. As initially conceived, the Petroleum Quality Analysis (PQA) system would include instrumentation mounted on a highly mobile platform to perform rapid analysis of POL. The current level of development in analytical chemistry is such that a small collection of commercially available analytical instruments, portable testers, and computer software could be used as an interactive unit to provide the required POL quality information at or near the point of end use. The collection of equipment will be transportable--when possible, some parts will be portable--and will permit the timely assessment of the quality of received, found, or captured fuels before being used by the Army. During fuels testing, the PQA system would identify specific fuel types and their quality. If needed, recommendations for corrective actions would also be provided by the data analysis software. As presently conceived, the system will not extend to meet full fuel purchase specification conformance testing requirements. The initial efforts for the design of the system are aimed at defining the best technical approach for the analysis of fuels. It is planned to include capabilities for the analysis of other POL at a later date.

## **II. OBJECTIVE**

The objective of this project was to identify the best technical approach to meet the requirements of the U.S. Army Petroleum Quality Analysis (PQA) system. The PQA system will replace the archaic fuels and lubricants analysis system currently in use and will employ alternative, state-of-the-art analytical techniques and methodologies to perform the necessary analyses.

## **III. APPROACH**

This project builds on earlier efforts to define PQA requirements and possible solutions to those requirements.(2) Currently required analyses are defined in MIL-HDBK-200G. These requirements were examined and evaluated to determine which ones should be retained in the PQA system. Where possible, alternative methods for each test were identified, keeping in mind

the requirements and constraints of the PQA system. Finally, a recommended approach to accomplishing the needs of the PQA system was compiled.

#### **IV. MIL-HDBK-200G: QUALITY ASSURANCE/QUALITY CONFORMANCE TESTING REQUIREMENTS**

The MIL-HDBK-200G is a "quality surveillance handbook for fuels, lubricants and related products."<sup>(1)</sup> It is considered the present foundation and starting point from which future POL analytical requirements should be developed. The handbook defines the specification and use limits for the various products and the acceptable analytical procedures that must be implemented by "properly trained personnel...to protect original product quality."<sup>(1)</sup> The handbook classifies the tests into four categories, corresponding to four levels of effort.

In TABLE 1, a summary of measurements specified by MIL-HDBK-200G is given for aviation and automotive gasolines and for turbine and diesel fuels. The table also includes the requirements defined for the four levels of analytical effort included in MIL-HDBK-200G. The significance of the various fuel properties or tests <sup>(3)</sup> is briefly discussed in the trade-off analysis section of this report.

"Type A" tests (not included in MIL-HDBK-200G) are the complete set of quality assurance, quality conformance, or specification inspection tests. Requirements for specific products are described only in the various fuels' specifications, as the following illustrates:

- MIL-G-3056 Gasoline, Automotive, Combat;
- MIL-T-5624N Turbine Fuel, Aviation, Grades JP-4 and JP-5 and JP-5/JP-8 ST special test fuel;
- MIL-T-83133C Turbine Fuel, Aviation, Kerosene Types, Grades JP-8 (NATO F-34) and NATO-F35;

**TABLE 1. Summary of Required Tests as Specified in MIL-HDBK-200G**

Property	POL Application by Test Category			
	Aviation Gasoline	Automotive Gasoline	Turbine Fuel	Diesel Fuel
Acid Number	--	--	--	2*
Accelerated Stability	--	--	--	2
Appearance	--	123C	--	123C
Carbon Residue	--	--	--	12
Cetane Index	--	--	--	2
Cloud Point	--	--	--	2
Color	123C	123C	123C	123C
Conductivity	--	--	123**	--
Corrosion	123	23	123	2
Density/Gravity	123C	123C	123C	123C
Distillation	123	123	123	12
Existent Gum	12	--	123	--
Filtration Time	--	--	123	--
Flash Point	--	--	123C	123C
Freezing Point	--	--	123	--
Fuel System Icing Inhibitor	--	--	123	--
Gum, Unwashed	--	23	--	--
Knock Rating	--	12	--	--
Lead	12	3	123†	--
Lean Mixture Rating	12	--	--	--
Oxidation Stability	--	2	--	--
Particulates	123	--	123	12
Peroxides	--	--	2	--
Potential Gum	2	--	--	--
Pour Point	--	--	--	2
Rich Mixture Rating	12	--	--	--
Sulfur	--	--	2	--
Thermal Stability	--	--	2	--
Vapor Pressure	12	12	123**	--
Viscosity	--	--	--	2
Water Separation Index	--	--	123	--
Water Reaction	123	--	123	--
Water and Sediment	--	--	--	2
Water and Solids	123C	123C	123C	--
Water Tolerance‡	--	123	--	--

\* Test Categories:

- 1 Type B-1 test
- 2 Type B-2 test
- 3 Type B-3 test
- C Type C test

\*\* JP-4 only

† Only if contamination is suspected

‡ Gasohol only

- MIL-F-46162C Fuel, Diesel, Referee Grade;
- VV-F-800E Fuel Oil, Diesel.

"Type B-1" tests demand partial analysis comprising the determination of principal characteristics most likely to have been affected in the course of moving the product. "Type B-2" tests specify partial analysis to verify characteristics describing product deterioration due to extended storage or age. "Type B-3" tests concentrate on partial analysis for contamination, in particular, for controlling the reinjection of pipeline interface products. "Type C" tests include the execution of basic (minimal) analyses to ascertain gross acceptability criteria. "Type C" tests consist of such measurements as specific gravity, color, and appearance, including visible sediment and water.

According to a concept statement--an initial "organizational and operational, or O&O, plan" (4)--by the Quartermaster School for automated petroleum testing capabilities in the battlefield environment, there are three testing systems corresponding to three areas of operation, as follows:

- Tactical testing at forward areas - Equipment should be man-portable and be limited to aid fast and simple go/no-go decisions.
- Operational testing - This allows for the use of a limited number of tests that would be performed on sophisticated, transportable equipment. Operators of this equipment would be "school-trained petroleum laboratory specialists (who) will perform B/C level tests, interpret results, and provide expert opinion on petroleum products." (4) Due to increased capability and sophistication, such laboratories would be able to provide improved precision and reliability of data and recommendations. The analytical equipment would be housed in trailers or transportable modules.
- Theater level testing - This testing system would provide the most comprehensive analyses, interpretation, and recommendations for the commanders. In future scenarios, analyses of petroleum products would be performed using a battery of state-of-the-art

equipment interfaced with a computer-based expert system. This level of testing would be performed in portable shelters.

## **V. REDEFINING THE REQUIREMENTS OF MIL-HDBK-200G**

The requirements given in MIL-HDBK-200G have worked reasonably well since the handbook was first published. The test methods specified to measure fuel quality are, for the most part, well established, useful, and familiar to Army fuel supply and handling personnel. However, these same test methods often are tedious, messy, labor intensive, and slow. They require large amounts of sample, produce large quantities of waste, and generally, do not use state-of-the-art methodologies and equipment to assure high analytical efficiency and accuracy. In addition, many of these test methods can be performed only in large, expensive laboratories that are difficult to transport. Modern analytical chemistry techniques can, in many cases, provide equivalent or improved information more conveniently and more accurately in less time, closer to the point of use, and with less sample in a more environmentally acceptable manner.

Potential conflict is encountered because Army fuel handling personnel must follow the requirements as listed in MIL-HDBK-200G. As currently written, these requirements are based on ASTM or Federal test methods. Very few of these methods require or allow the use of automated test equipment or secondary methods that base their results on calculation and estimation. This means that if the requirement is specified in MIL-HDBK-200G, it must be strictly followed, thereby restricting Army petroleum specialists to the use of older, slower, manual, and often obsolete methods.

It is reasonable to assume that the end user of a fuel is interested in knowing only that the fuel is suitable for use in a given vehicle. The user is rarely concerned about the process involved in determining the fuel's suitability. Assuming this, the requirements in MIL-HDBK-200G should be redefined to allow the use of modern analytical techniques to derive the necessary information to determine the suitability of a given fuel. In some instances, the new requirements would likely be very similar to the old. For example, a new, smaller, pass/fail flash point tester could be

specified to replace the older Pensky-Martens closed cup, flash point testing apparatus. The resulting information would be the same; the two techniques are nearly equivalent. In other instances, the new requirements would vary considerably from the old. Estimated aromatics content from infrared (IR) spectroscopy could replace the fluorescent indicator adsorption method (ASTM D 1319). The new test is faster and actually provides more reliable results.

Applying this concept to the entire slate of tests currently listed in MIL-HDBK-200G could result in a smaller, more informative set of requirements. The newer set of tests would take less time to perform, use less sample, produce less waste, and provide equivalent information (not necessarily equivalent fuel properties). The results could easily be directed to a computer for additional analysis, interpretation, fuel use recommendations, or archival storage. The results could also be transmitted via satellite linkage to designated commands.

Excellent correlations have been developed and are being improved between fuel properties as measured by ASTM and other accepted methods, and spectroscopic analyses. For example, the total sulfur content of a fuel is rarely measured by the older lamp sulfur or bomb sulfur/barium sulfate precipitation procedure. Rather, most laboratories use instrumental analytical methods based on atomic absorption, X-ray fluorescence, or inductively coupled plasma spectroscopies. Most automated or automatic equipment designed for fuel property measurements give comparable or improved description of the sample as compared to the original, manual procedures.

Instrumental analytical correlations have been and are being developed to provide excellent estimates of various fuel properties. In these procedures, a spectroscopic technique, usually based on near or midband infrared spectroscopy, is used to record the spectra for a set of calibration (training) fuels. The fuels' spectra, along with their known property data, are used to calculate calibration files for the infrared spectrometer. The infrared spectrum of an unknown fuel can then be used, in conjunction with the calibration file, to estimate selected properties of the fuel. In many instances, the estimated property values are of sufficient accuracy and precision to be useful to the end user of the unknown fuel. (A more detailed discussion of the use of infrared spectroscopy to estimate fuel properties is found in the appendix.)

While many of these secondary (estimation) methods have yet to receive the approval of ASTM or similar sanctioning bodies, their eventual acceptance is expected. Those correlations that provide acceptable estimates of data and are comparable to those derived by sanctioned (e.g., ASTM) procedures could be used to advantage in PQA. If such correlations were used in the PQA system, then together with other selected procedures, the PQA system would be a modern, viable system for the required analysis of fuels.

## **VI. BRIEF DESCRIPTION OF MIL-HDBK-200G TEST METHODS**

In TABLE 2, a summary is given of the methods currently used to measure the fuel properties required by MIL-HDBK-200G. In those cases where a specific method is not listed in the handbook, the generally accepted method is listed in the table. Additionally, the table provides a reminder of the basic steps of the procedure used (under "Summary of Procedure"), the usual time required to perform a single measurement by that procedure, and the approximate commercial cost to perform the analysis. An indication is also given of those fuel properties that may be correctly estimated by secondary methods, e.g., through infrared spectroscopy. Note that data derived from infrared spectroscopy are not restricted to those listed, and all fuel properties that are part of the infrared calibration file are determined simultaneously within approximately one minute using 1 to 10 ml of fuel.



TABLE 2. Description of ASTM Test Methods Currently Used to Measure Fuel Properties

Property	Specified ASTM D Methods	Usual ASTM D Methods of Measurement	Summary of Procedure	Time Required to Perform a Single Measurement, min	Typical Cost Per Analysis*	Data Derived From Infrared (IR) Spectroscopy
Acid Number	N**	974, 3242	Titration	30	49	NEG†
Accelerated Stability	N	2274	Heat w/air, weigh	150	398	NEG
Appearance (Visual)	N	4176	Visual	10	26	NEG
Carbon Residue	N	189	Dist., burn, weigh	120	51	UNK‡
Cetane Index	N	976	Calc. (density, dist.)	15	20	POS§
Cloud Point	N	2500	Cool, observe	30	50	POS
Color	2392, 1500	1500	Compare	15	17	NEG
Conductivity	2624	3114	Meter	15	61	NEG
Corrosion	130	130	Heat, compare	60	40	NEG
Density/Gravity	N	1298	Meter	15	25	POS
Distillation	86	86	Heat, observe, plot	90	53	UNK
Existent Gum	381	381	Evaporate, weigh	60	110	NEG
Filtration Time	2276	2276	Timed filtration	90	65	NEG
Flash Point	56, 93	93	Heat, observe	90	50/39	POS
Freezing Point	N	2386	Cool, observe	30	98	POS
Fuel System Icing Inhibitor	5006	5006	Extract, measure	60	100	POS
Gum, Unwashed	381	381	Evaporate, weigh	60	110	NEG
Knock Rating	2699, 2700	2699, 2700	Engine tests	60	108	POS
Lead	3341, 2787	3341, 2787	Titrate (discontinued)	--	--	NEG
Lean Mixture Rating	909	909	Engine test	--	--	UNK
Oxidation Stability	N	525	Heat w/oxygen	120	144	NEG
Particulates	2276	2276, 5254*	Filter, weigh	90	63	NEG
Peroxides	3703	3703	Titrate	45	133	NEG
Potential Gum	N	873	Heat, weigh	180	195	NEG
Pour Point	N	97	Cool, observe	90	40	POS
Rich Mixture Rating	909	909	Engine test	--	--	UNK
Sulfur	1266, 2622	1266, 2622	Burn, XRF	30	36	NEG
Thermal Stability	N	3241	JFTOT	210	280	NEG
Vapor Pressure	323, 2551	323, 2551	Heat, measure	60	65	NEG
Viscosity	88	445	Timed flow	30	28	POS

TABLE 2. Description of ASTM Test Methods Currently Used to Measure Fuel Properties, Cont'd

Property	Specified ASTM D Methods	Usual ASTM D Methods of Measurement	Summary of Procedure	Time Required to Perform a Single Measurement, min	Typical Cost Per Analysis	Data Derived From Infrared (IR) Spectroscopy
Water Separation Index	2550	3948	Instrumental, microsep.	30	118	NEG
Water Reaction	N	1094	Mix and observe	60	37	NEG
Water and Sediment	2709	2709	Centrifuge, measure	60	79	NEG
Water and Solids (Visual)	N	4176	Visual	15	26	NEG
Water Tolerance	N	4814	Cool and observe	60	102	NEG

\* Commercial rates

\*\* Not specified

† NEG = Not expected

‡ UNK = IR correlations may exist

§ POS = IR correlations exist or are expected

★ D 5254 is the current laboratory method for measuring particulate content.

## VII. TRADE-OFF ANALYSIS

The following is a discussion of each of the fuel properties specified in MIL-HDBK-200G. Included in this discussion is a description of the test method currently used to determine each property and a list of possible alternatives, if they exist. This discussion is based upon MIL-HDBK-200G requirements, experience gained in recent military conflicts, and advances in analytical chemical knowledge and equipment. Recommendations are based on present and anticipated future military requirements and methodologies to satisfy those requirements. In addition, the following items were considered to be constraints on the PQA, as described in the Operational Requirements Document (5):

- Perform testing on each test device simultaneously with one sample or with multiple samples at once per device.
- Be self-contained and operate for a minimum of 30 days. Analyze a minimum of 15 samples per day without resupply of expendable supplies with the exception of those expendable supplies found commonly throughout the theater (e.g., water and fuel).
- Be ruggedized so it will be operable on a vehicle with adequate mobility to move forward of the Forward Support Battalion under cross-country conditions.
- Operate 16 hours per day (required), 20 hours per day (desired).
- Operate by two soldiers (required), one soldier (desired), in MOS 77L.
- Require no more than a 3-Kw generator to operate when not mounted on a vehicle. When installed on a vehicle, the PQA will operate using the vehicles' electrical system. It will have a battery that will allow one full test cycle to be performed in the event of a power failure.

- Be fully operational within 30 minutes of arrival on station and deployable 20 minutes after completion of sample processing.
- Survive biological and chemical attack to the ability of the host vehicle when not in use.

The application of the above constraints to the PQA system leads to the following restrictions:

- The PQA cannot contain any type of test equipment which requires large amounts of power or would require more than 30 minutes to warm up or in some other way become functional. This restriction eliminates oil baths, water baths, gum blocks, heating blocks, and other types of high-wattage, resistance-heated equipment.
- The ruggedization requirements eliminate the use of an analytical balance.
- If a venting system is required to remove unwanted fumes, it must not allow biological or chemical warfare agents to enter the enclosure. This eliminates conventional fume hoods from inclusion in the PQA. Owing to the projected small space of the enclosure, any tests which generate relatively large amounts of fumes should not be included in the PQA.
- Owing to the increased mobility requirements of the PQA system, it is unlikely that a total test time of greater than 30 minutes for any given sample would be acceptable.
- Since the PQA is required to analyze a minimum of 450 samples without resupply of expendables, analyses (e.g., acid number) which require greater than 10 mL of solvent exert a logistical strain on the PQA. These tests are probably best left out or replaced with an alternative technique.

## **A. Fuel Property Measurement Methods**

The following section gives a critical evaluation of fuel property measurement methods that are specified in MIL-HDBK-200G.

### **1. Acid Number**

The test procedure currently specified to measure this property is ASTM D 974, "Standard Test Method for Acid and Base Number by Color-Indicator Titration." This method covers the determination of acidic or basic constituents in petroleum products and lubricants. It is applicable for the determination of acids or bases whose dissociation constants in water are larger than  $10^{-9}$  (extremely weak acids or bases do not interfere). Acid number may indicate gross fuel degradation, the presence of some sulfur-containing contaminants, or sabotage agents.

Since the D 974 procedure is based on a color-indicator titration, it would be difficult to automate. ASTM D 664, "Standard Test Method for Acid Number of Petroleum Products by Potentiometric Titration," is simple to automate using an automatic titrator. The use of automatic titrators for potentiometric titrations is a well-developed technology. Several laboratory instrument manufacturers sell automatic titrators which could be used for this test. Most modern automatic titrators are designed to interface to a computer for control and data collection. Approximate price for a titrator to determine acid number is \$7,500. The use of an automatic titrator will not significantly reduce the analysis time of approximately 25 to 30 minutes. Currently available titrators take up less than 3 to 4 cubic feet of space and weigh less than 25 pounds. These titrators are not sufficiently ruggedized to meet the requirements of the PQA. The cost to ruggedize the instrument is not known.

The sample size for a determination is approximately 15 to 20 mL added to 125 mL of titration solvent. Buffers and titration solutions are also required to conduct this test. In total, each analysis generates approximately 150 mL of waste consisting of water, isopropyl alcohol, toluene, potassium hydroxide, trimethyl pyridine, m-nitrophenol, and various buffers.

**Recommendation:** It is recommended that determination of acid number not be included in the PQA. The test is slow, requires further development to meet PQA needs, generates significant waste, and analyzes for a fuel property that usually changes little from refinery to end use. However, it should be noted that acid number can increase during long periods of storage, and fuels of opportunity could have elevated acid content. In some cases, other fuel properties such as viscosity or color will worsen as the acid number of the fuel increases. Therefore, measurement of these properties will relate to the fuel's acidity.

## 2. Accelerated Stability

The current test method used to determine this property is D 2274, "Standard Test Method for Oxidation Stability of Distillate Fuel Oil (Accelerated Method)." The results of this test give an indication of the tendency of the fuel to form fuel-insoluble residues at some point in the future. The correlation of the results of this test to actual fuel storage in the field is unproven and variable. Fuel in storage is subject to interactions with the storage environment, which are not included as part of the accelerated test. Under the conditions of this test, a 350-mL volume of the fuel is prefiltered and aged at 95°C for 16 hours. Oxygen is bubbled through the sample during the aging.

Many accelerated fuel stability tests do exist. The aging times range from 90 minutes to 2 years. All require aging the fuel at an elevated temperature that must remain constant throughout the aging period. In addition, most fuel stability tests require some additional testing (e.g., filtration, color, gum determination, etc.) of the aged sample. Each of these work-up procedures requires additional support and generates additional waste. With the possible exception of the 150°C, 90-minute aging test, none of the currently used accelerated stability tests lends itself well to inclusion in the PQA.

**Recommendation:** It is recommended that a test for accelerated stability not be included in the PQA. The cost and logistical requirements are high, and the results of the test are imprecise and meant to estimate fuel quality at some future date. Additionally, all currently accepted test methods require at least 90 minutes of aging which is unacceptable for inclusion in the PQA.

### 3. Appearance

This fuel property is determined by a visual examination of the sample to evaluate the workmanship, stability, and contamination in terms of free water, sediment, and suspended matter. The analyst pours a portion of the sample to be examined into a clean, clear container and holds the container to the light for examination. This is a widely accepted test; however, the results are quite subjective. An automated test ("numerical clean and bright") exists which is less subjective but is also less widely used and accepted. The automated test uses the microseparometer which is part of the determination of water separability. The microseparometer uses approximately 50 mL of fuel. The cost of the microseparometer is approximately \$15,000. Each analysis with the microseparometer also requires a disposable "alumicell" at a cost of \$10 to \$15. The microseparometer could be integrated into a computer controlled network.

**Recommendation:** It is recommended that a manual test for visual appearance be included in the PQA. Although the results are subjective, an experienced analyst can tell much about a fuel from a visual examination. The numerical clean and bright test should be included only if the microseparometer is included for determination of water separability.

### 4. Carbon Residue

This property is currently determined using ASTM D 524, "Standard Test Method for Ramsbottom Carbon Residue of Petroleum Products." Carbon residue is intended to provide some indication of the product's relative coke-forming propensity. Under the conditions of the test, the sample is weighed into a special glass bulb and placed in a furnace at 550°C. The bulb remains in the furnace for 20 minutes after which it is removed, cooled, and reweighed. An extra sample preparation step is required when testing fuels of grades 1 and 2. For these lighter fuels, a 200-mL sample of the fuel is distilled until only 10 volume percent of the original fuel sample remains. The actual carbon residue test is then conducted on the 10-percent distillation residue.

A microcarbon residue tester is currently available and could be used to determine carbon residue. This method would not require a large furnace but would still require an analytical

balance. Additionally, the results of the microcarbon method correlate better to the Conradson carbon test, not the Ramsbottom method.

Preliminary evaluations have shown that infrared (IR) spectroscopy, combined with multivariate statistics, may be able to estimate the carbon residue of a fuel.

**Recommendation:** It is recommended that the analysis for carbon residue be included in the PQA only if it can be estimated by IR. Since IR has the potential to estimate many fuel properties simultaneously, it will likely be included in the PQA. It remains to be determined if a reliable calibration model for carbon residue can be developed. It should be noted that the carbon residue level of a given fuel is not likely to significantly change between production and use unless it is contaminated. This type of contamination could probably be detected through other means such as distillation.

## 5. Cetane Number (Cetane Index)

Cetane number is determined by the ASTM D 613, "Standard Test Method for Ignition Quality of Diesel Fuels by the Cetane Method." This test method uses an engine test that requires approximately 800 ml of fuel. It is not feasible to consider the inclusion of the cetane number test into the PQA; the cost, space requirements, and logistical support are too great. Because of the relative nonavailability of the cetane test, several methods have been developed to estimate cetane number from other fuel properties. This estimated (calculated) cetane number is known as cetane index. The two most commonly used calculation methods are D 976, "Standard Test Methods for Calculated Cetane Index of Distillate Fuels" and D 4737, "Standard Test Method for Calculated Cetane Index by Four Variable Equation." Both of these methods use fuel density and distillation data to estimate cetane number. Either one, or both, could be included on the computer in the PQA to provide cetane index (assuming that the required data for the calculation are available). D 976 is the method currently specified in VV-F-800 (diesel fuel) and MIL-T-83133 and MIL-T-5624 aviation kerosene fuels.



Cetane number is related to the composition of the fuel. For example, a fuel will have higher cetane number if the *normal*- to *iso*-paraffin ratio is increased, while increased aromatic hydrocarbon concentrations decrease cetane number. Because of such relationships, cetane number can be estimated using instrumental techniques such as infrared spectroscopic analysis. The use of infrared techniques is gaining continual acceptance as a means to estimate cetane number. A drawback of the infrared spectroscopic, non-engine methods is that they may not reflect the improvement in ignition quality with the addition of ignition improver additives, i.e., the effect of cetane number improvers on infrared-estimated cetane number is unknown at this time. However, FTIR shows promise, since it can quantitatively measure nitrate-type ignition improver additives at concentrations commonly used in middle distillate fuels.

**Recommendation:** Estimation of cetane number through IR spectroscopy should be included in the PQA. Cetane index, calculated from density and distillation data, may contain larger error. Therefore, this value should not be included in the PQA.

## 6. Cloud Point, Freeze Point, Pour Point

Cloud point is measured by D 2500, "Standard Test Method for Cloud Point of Petroleum Products." Freeze point is measured by D 2386, "Standard Test Method for Freezing Point of Aviation Fuels." Pour point is measured by D 97, "Standard Test Method for Pour Point of Petroleum Products." These three properties help define low temperature operability characteristics of fuels. Cloud point is the temperature at which wax crystals appear in the fuel. Freezing point is the lowest temperature at which the fuel remains free of solid hydrocarbon crystals. Pour point is the lowest temperature at which movement of the fuel specimen is observed. In normal practice, all three of these test methods use baths filled with dry ice and alcohol to cool the sample at a prescribed rate. The inclusion of this test in the PQA is not feasible due to the requirements to maintain large volumes of alcohol and a ready supply of dry ice.

Automated methods are available for these tests. Essentially, the automated tests duplicate the manual tests using robotic devices to perform the sample movement. These test methods are not suitable for the PQA for the same reasons as the manual method.

Automatic testers are also available for these tests. These testers use piezo-electric cells to cool the sample and light scattering to detect the presence of wax crystals or movement. These testers require only a standard power source and can perform all three tests. The cost of an automatic tester is approximately \$70,000. The primary drawback to this approach is that the automatic testers still follow the prescribed cooling rate for the manual methods. Consequently, the time needed to complete the three analyses, depending on the characteristics of the fuel, can be as long as 2.5 hours. Running just one of the tests can take as long as 45 minutes. These test times do not fit well with the requirements in the PQA system.

Preliminary testing has shown that IR methods should be able to reliably estimate the cloud and freeze points of a given fuel. Pour points will be more difficult owing to the possible presence of pour point depressant additives. Additional testing is required to develop correlation models for these properties.

**Recommendation:** A manual method for the measurement of cloud point, freezing point, and pour point is not feasible for inclusion in the PQA. It is recommended that the appropriate IR calibration models be developed and used to estimate these properties.

## **7. Color**

Two tests are currently used to measure the color of a fuel. The color of kerosene fuels is measured by ASTM D 156, "Standard Test Method for Saybolt Color of Petroleum Products," and the color of diesel fuels is determined by ASTM D 1500, "Standard Test Method for ASTM Color of Petroleum Products (ASTM Color Scale)." Both of these test methods perform adequately and could probably be included in the PQA were it not for the growing use of dyes in fuels as a part of governmental regulation and taxing. Fuels currently available to the Army are either undyed or contain dye such as red dye, blue dye, green dye, or combinations of each.

Additionally, undyed diesel fuel can also have a color ranging from colorless (water white) to yellow to red to dark brown. The addition of a dye to a fuel with color only complicates the measurement of the color of the fuel. The measurement of the color of a dyed fuel, using the standard color scales in D 156 and D 1500, is meaningless since neither of these scales was developed using dyed fuels. ASTM is currently investigating this problem and will be working toward the development of standardized tests for the color of dyed and undyed fuels.

An automatic tester, using a tri-stimulus method, is available and has been shown to correlate well with D 156 and D 1500 results. It has yet to be fully evaluated with dyed fuels. The cost of this tester is approximately \$10,000.

**Recommendation:** Until an appropriate method of measuring dyed fuels is developed, it is recommended to use visual inspection of the fuel to determine signs of contamination.

## 8. Conductivity

The conductivity of a fuel refers to its ability to dissipate electrical charges within the fuel. Addition of conductivity additives to turbine fuels helps assure that static electrical charges (e.g., static charges due to high-speed fueling operations) will not accumulate to cause sparks and possible explosion of the fuel tank. The test method currently specified to determine conductivity is D 2624, "Standard Test Method for Electrical Conductivity of Aviation and Distillate Fuels." Under this test method, a voltage is applied across two electrodes in the fuel, and the resulting current is expressed as a conductivity value. The combination of increased Army use of JP-8 and the move to more rapid refueling (such as with the Standard Army Refueling System), along with the possibility of accumulated static charges in the fuel, dictate a need to be able to assess fuel fire safety through determination of fuel conductivity.

**Recommendation:** This fuel property must be measured by applying a current across two electrodes. Currently, there is no known alternate method to measure conductivity. Method D 2624 allows the use of portable meters which are readily available and reasonably priced. It is recommended the PQA system include a portable conductivity meter.

## 9. Corrosion

ASTM D 130, "Standard Test Method for Detection of Copper Corrosion from Petroleum Products by the Copper Strip Tarnish Test," is used to assess the relative degree of corrosivity of a fuel. This corrosivity is normally caused by the presence of certain types of sulfur compounds in the fuel. In this test, a polished copper strip is immersed in a given quantity of fuel and heated to 100°C for a period of 90 minutes. At the end of the heating period, the strip is removed and washed, and its appearance is compared to a set of copper corrosion standards.

It is not likely that the PQA would include the copper strip corrosion test because of the power requirements for the heating bath. Additionally, fuels that fail this test are rare due to modern refining practices and reduced fuel sulfur levels. It should be acceptable for most fuels to simply determine the total sulfur content of the fuel. Fuels with sulfur levels below 0.3 mass percent will normally be acceptable. Fuels with total sulfur above 0.3 mass percent could be considered suspect and eligible for additional testing at a laboratory with full ASTM testing capability.

**Recommendation:** Because of the larger logistical and power requirements of D 130 and the very low rate of fuel failures with this test, it is recommended that copper corrosion by D 130 not be included in the PQA.

## 10. Density/Gravity

Density/gravity is the measure of the weight per unit volume of the fuel. These values are fairly diagnostic for fuel grades (e.g., gasolines, aviation turbine fuels, and diesel fuels have increasing densities). Density is usually measured with a pycnometer, a hydrometer, or a density meter. The pycnometer gives a high degree of accuracy but is an involved procedure and requires the use of a balance. With this method, a small glass container with a known volume is filled with fuel expelled from a syringe. The container is then weighed on an analytical balance.

The hydrometer method is less accurate than the pycnometer method. In this procedure, approximately 400 mL of fuel is poured into a cylinder, and a glass hydrometer is placed in the

fuel. A reading is taken from the hydrometer at the meniscus of the fuel, and at the same time, fuel temperature in the cylinder is recorded. The hydrometer and temperature readings are used to enter a table of conversions, and the density or gravity of the fuel is calculated.

A density meter can potentially give the most accurate measurement in the least amount of time. A typical analysis with a high precision of accuracy, the bench top meter takes approximately 8 to 10 minutes. Small, handheld meters are also available to measure density. The analysis time with these meters is less than one minute. In general, the handheld meters provide one order of magnitude lower accuracy than any of the other methods (i.e., they are accurate to three places instead of four).

Infrared spectroscopy has also been proven to accurately estimate the density of diesel fuels.

**Recommendation:** The PQA should use infrared spectroscopy to measure fuel density.

## **11. Distillation**

The distillation properties of a fuel roughly classify the product into categories (e.g., gasoline, turbine fuel, diesel fuel, etc.) according to molecular weight and volatility. Distillation relates to the fuel's tendency to vapor lock; it may indicate the presence of low molecular weight contaminants (e.g., as in gasoline) or high molecular weight contaminants (e.g., as in residual fuel). Results of distillation may also be linked to the product's heat of combustion, flash point, and viscosity. Distillation is determined using ASTM D 86, "Standard Test Method for Distillation of Petroleum Products." A 100-mL sample is distilled under prescribed conditions. Systematic observations of thermometer readings and volumes of condensate are made and used to calculate the results.

Because the distillation properties of a fuel provide so much information about the fuel and relate to so many engine operability parameters, it is important that the PQA system have a means to carry out distillation. However, both manual and automatic distillation units, as described in

D 86, have significant power requirements, and the D 86 method is time-consuming and involved.

ASTM D 2887, "Standard Test Method for Boiling Range Distribution of Petroleum Fractions by Gas Chromatography," provides a possible alternative to the D 86 distillation. This method uses a fairly standard gas chromatograph and column, both commercially available. The software utilized in the data acquisition and calculations is also easily accessible. The cost of a system for D 2887 ranges from \$20,000 to \$40,000. However, the maintenance and calibration of this equipment is also involved and time-consuming. The typical analysis time for this test is 30 to 45 minutes, depending on the fuel.

Distillation data, especially the high-end information, should be readily obtainable from infrared spectra. This method is probably the best approach for the PQA system.

**Recommendation:** Because distillation characteristics provide so much useful information, it is imperative that the PQA provide a means to determine distillation characteristics. The preliminary results indicate that infrared is able to reliably estimate the high-end distillation characteristics of a fuel. If it is later determined that infrared cannot provide useful distillation information, then some other means, such as gas chromatography, should be included in the PQA system.

## 12. Existent Gum

Existent gum is determined by ASTM D 381, "Standard Test Method for Existent Gum in Fuels by Jet Evaporation." Also referred to as air jet gum, steam jet gum (in diesel fuels), and washed and unwashed gum, existent gum is the amount of nonvolatile, heptane-insoluble residue present in a fuel, as measured under the conditions of the test. Existent gum may indicate the presence of some additives or the fuel's tendency to form deposits. Existent gum has never been shown to have any direct correlation to the stability characteristics of a fuel. Under this test, a measured quantity of fuel is evaporated under controlled conditions of temperature and flow of air or steam. The residue is weighed and reported.

The PQA would not be able to support the direct determination of existent gum. The size and power requirements of the gum apparatus are well beyond the constraints of the PQA system. Preliminary calibration efforts have yielded very poor results when using infrared spectroscopy to estimate the existent gum content of fuels.

**Recommendation:** In general, this property provides little useful information to the end user of a fuel. It is recommended that the test for existent gum be included in the PQA system only if this property can be successfully estimated using infrared spectroscopy. Otherwise, existent gum should be left out of the PQA.

### 13. Flash Point

The flash point of a fuel is the lowest temperature to which the fuel must be heated to produce an ignitable vapor-air mixture above the liquid fuel when the fuel is exposed to an open flame. Flash point is important from a fuel handling standpoint. Too low a flash point will cause fuel to be a fire hazard. Flash point can also indicate contamination. A diesel fuel with an unusually low flash point may indicate contamination of the diesel fuel with more volatile components such as gasoline. The flash point of a diesel fuel has no significant relation to its operation in the engine.

The most commonly used method for flash point is ASTM D 93, "Standard Test Methods for Flash Point by Pensky-Martens Closed Tester." In these tests, the sample is heated at a slow, constant rate with continual stirring. A small ignition source is directed into the cup at regular intervals. The flash point is the lowest temperature at which application of the test flame causes the vapor above the sample to ignite. Both manual and automated apparatus are available to perform this analysis. Each of these flash point testers occupies about 1 cubic foot of bench space. To heat the sample and provide the ignition source, these testers require either an external gas supply or comparatively large amounts of electrical power, or some combination of the two.

Alternatives to D 93 include the use of smaller, portable, flash point testers such as the SetaFlash<sup>®</sup> tester, or the use of infrared spectroscopy, gas chromatography, or a combination of

the two methods. All preliminary testing has shown that infrared spectroscopy by itself is not sufficient to provide a reliable flash point estimation. An Army-sponsored project is currently studying the use of infrared spectroscopy combined with gas chromatography data to give a more reliable estimation of flash point.

The SetaFlash tester is commercially available and is rugged enough to be included in the PQA system. A 12-volt battery powers the heater, and a refillable, self-contained gas cylinder supplies the ignition source. Another attractive feature of this tester is that it can be set to test as pass/fail at any given temperature.

**Recommendation:** The PQA should contain a SetaFlash flash point tester. The tester should be set to operate in the pass/fail mode at the specified flash point for the grade of fuel being tested. If a reliable method is developed to estimate flash point using infrared spectroscopy and gas chromatography, is developed, that method could replace the SetaFlash tester.

#### **14. Fuel System Icing Inhibitor**

The only approved Fuel System Icing Inhibitor (FSII) for diesel fuel is diethyleneglycol monomethylether (di-EGME). FSII is added to fuel at a treatment rate of 0.15 volume percent. When it is added to the fuel, it preferentially partitions to any free water in the fuel system. The FSII lowers the freezing point of the water and thereby reduces the chance of ice crystal formation which can plug fuel lines, screens, and filters. This is an important test to conduct on fuel for aviation use but is not as important for fuel intended for ground vehicle use.

The concentration of FSII in a fuel is determined by extracting the FSII from the fuel with a specified volume of water. The refractive index of the water is then measured and compared to a standard calibration chart to determine FSII concentration. A titration method is also available as part of the ASTM specification for FSII compounds. Both of these methods would require unacceptable logistic support and would generate comparatively large amounts of hazardous waste.



As an alternative, it is expected that infrared spectroscopy will be able to adequately measure the level of FSII in a fuel, although this project is not yet complete.

**Recommendation:** It is recommended that the PQA system use infrared spectroscopy to determine FSII levels in unknown fuels.

#### 15. Knock Value or Octane Number

Octane number is a gasoline performance characteristic for spark ignition engines that indicates if the fuel will burn progressively by the spark-initiated flame front without preignition or uncontrolled detonation. Octane number is determined by ASTM D 2699, "Standard Test Method for Knock Characteristics of Motor Fuels by the Research Method," and ASTM D 2700, "Standard Test Method for Knock Characteristics of Motor and Aviation Fuels by the Motor Method." Both methods employ a specialized test engine, use approximately 1 liter of fuel, and take 20 to 30 minutes to conduct. The space and power requirements for the test engine are too large to consider for inclusion in the PQA system. The necessity of including measurement of octane number in a PQA is further reduced since the Army uses very little gasoline as a mobility fuel.

As an alternative, infrared spectroscopy has proven to give very reliable estimations of octane number.

**Recommendation:** Since an infrared spectrometer will likely be included in the PQA system, it is recommended that an appropriate calibration model be developed to allow estimation of octane number.

#### 16. Lean Mixture Rating and Rich Mixture Rating

These two properties are gasoline performance properties. Rich mixture rating refers to the maximum performance available from an aviation gasoline. Lean mixture rating relates to steady state, or cruising, requirements. They are measured by ASTM D 909, "Standard Test Method

for Knock Characteristics of Aviation Gasolines by the Supercharge Method." Like the octane number tests, these methods use a specialized test engine.

Although it has yet to be proven, it is possible that infrared spectroscopy could be used to estimate these two properties.

**Recommendation:** It is recommended that little emphasis be placed on these properties since they are specific to aviation gasoline. The PQA system does not have the space or power capacity to include a test engine for these properties. If aviation gasoline requirements are eliminated, these measurements should be dropped. However, if determination of these properties becomes a requirement, the applicability of infrared spectroscopy should be investigated.

#### 17. Oxidation Stability

Oxidation stability refers to a product's tendency to remain unchanged during prolonged storage. Unstable fuels and lubricants tend to oxidize. The oxidized species then decompose to form various deposits on induction system manifolds, valves, etc. Oxidation stability of fuels is increased by antioxidant additives. This fuel property may be measured by ASTM D 525, "Standard Test Method for Oxidation Stability of Gasoline (Induction Period Method)." The fuel sample is oxidized in a high pressure reactor (bomb) under 100 pounds per square inch of oxygen in a water bath maintained at 98 to 102°C. Oxidation stability of the fuel is proportional to the measured induction period or the equivalent break point. The induction period or break point is the duration of time at which a rapid rise of oxidation rate occurs, as manifested by a well-defined, rapid loss of oxygen pressure.

As with other fuel stability tests, the oxidation stability of gasoline is meant to estimate the condition of the fuel at some time in the future. This makes the test an important one for specification testing and acceptance. However, this test is not applicable to determining whether a given gasoline is of sufficient quality for immediate use.

**Recommendation:** Since the PQA system cannot support the space and power requirements for the test apparatus or proper test procedure that may be applicable in the field, and because this fuel property refers to future rather than present usefulness of fuels, it is recommended that a test for this property not be included in the PQA system.

## **18. Particulates**

The currently specified test method for measuring particulates is ASTM D 2276, "Standard Test Method for Particulate Contaminant in Aviation Fuel by Line Sampling." This procedure is no longer applicable to the laboratory measurement of particulates in fuel. The current laboratory procedure is ASTM D 5452, "Standard Test Method for Particulate Contamination in Aviation Fuels by Laboratory Filtration." This is a gravimetric determination, by filtration, of particulate contaminant in a sample of aviation fuel. This method is not applicable to diesel and nonaviation kerosene fuels. A laboratory procedure for measuring the level of particulates in diesel fuel is currently under development within ASTM and should be available in approximately 1.5 to 2 years. However, this procedure requires the use of a large drying oven and an analytical balance, both of which are beyond the scope of the PQA.

An alternative procedure would involve the use of a fuel filterability test such as specified in ASTM D 2068, "Standard Test Method for Filter Blocking Tendency of Distillate Fuel Oils." In this procedure, the fuel is pumped through a test filter at a predetermined flow rate. A pass or fail result is dependent on successfully filtering a selected volume of fuel before the pressure drop across the filter reaches a given point. This test could be customized to Army requirements by selecting the type of test filter, the required volume of filtered fuel, and the cut-off pressure drop.

**Recommendation:** Since the required equipment for the laboratory particulates test are beyond the capabilities of the PQA, it is recommended that a fuel filterability test based on D 2068 be used to measure particulate content.

## 19. Sulfur

Sulfur can cause wear in diesel engines as a result of the corrosive nature of some sulfur compounds and their combustion by-products, and can increase the amount of deposits in the combustion chamber and on the pistons. Recent governmental regulations have set the allowable level of sulfur in diesel fuels for transportation at a maximum of 0.05 mass percent. As a result of this ruling, CONUS diesel fuels are generally low in sulfur contents. However, JP-8 is allowed to contain up to 0.30 mass percent sulfur, and OCONUS fuels could possibly contain as much as 1.0 mass percent or more. Because of the need to meet CONUS emissions regulations as well as the need to protect engines from higher sulfur levels in OCONUS fuels, the PQA system must contain a means to determine sulfur content.

Several test methods are approved for determining sulfur level in diesel fuels. ASTM D 129, "Standard Test Method for Sulfur in Petroleum Products (General Bomb Method)," is specified as the referee method. ASTM D 129 is a difficult and involved method to perform and, because of the space, time, and power requirements, would not be suitable for the PQA system. The most common method for sulfur analysis is X-ray fluorescence spectroscopy.

Currently, the only approved method for the analysis of low levels of sulfur (<0.05 mass percent) is D 2622, "Standard Test Method for Sulfur in Petroleum Products by X-ray Spectrometry." D 2622 involves the use of a wavelength-dispersive X-ray instrument. ASTM D 4294, "Standard Test Method for Sulfur in Petroleum Products by Non-Dispersive X-ray Fluorescence Spectrometry," is an alternative X-ray procedure using an energy-dispersive X-ray spectrometer. The cost of a wavelength-dispersive instrument is generally two to four times that of an energy-dispersive unit. Also, dedicated energy-dispersive sulfur analyzers are commercially available at a cost of less than \$20,000.

**Recommendation:** The PQA system must include the capability to determine the total sulfur level in fuels. The requirements for the manual methods of analysis are beyond the scope of the PQA system. An X-ray fluorescence spectrometer should be included in the PQA. Through careful choice of this instrument, the X-ray spectrometer could also be used to determine the

levels of other selected elements such as lead, iron, calcium, and others, depending on the detection limits.

## 20. Thermal Stability

Thermal, or high temperature, stability is measured on aviation jet fuel and other gas turbine fuels to rate the tendency of the fuel to form deposits within the fuel system. The test method used to determine this property is described in ASTM D 3241, "Standard Test Method for Thermal Oxidation Stability of Aviation Turbine Fuels (JFTOT Procedure)." This test method uses a specific instrument, the Jet Fuel Thermal Oxidation Tester (JFTOT), to perform the analysis. The fuel is pumped at a fixed volumetric flow rate through a heater after which it enters a precision stainless steel filter where fuel degradation products may become trapped. The test requires 600 mL of test fuel. The test duration is 2.5 hours.

**Recommendation:** This is an important fuel specification property and therefore, would be helpful to have this test available in the field. However, the space, power, and test time requirements for the JFTOT are beyond the scope of the PQA system. There is currently no known alternative method for measuring this property, and there has been no success with attempts to estimate this property through spectroscopic techniques. It is recommended that this property not be included in the PQA system.

## 21. Vapor Pressure

Vapor pressure is important for both automotive and aviation gasolines. It affects starting, warm-up, and tendency to vapor lock at high operating temperatures or high altitudes. Vapor pressure is also used as an indirect measure of the evaporation rate of volatile petroleum solvents. There are at least eight different methods for determining vapor pressure, depending on the type of sample being tested. The most familiar test, and the procedure specified in MIL-HDBK-200G, is ASTM D 323, "Standard Test Method for Vapor Pressure of Petroleum Products (Reid Method)." Under this procedure, the liquid chamber of the vapor pressure apparatus is filled with the chilled sample and connected to the vapor chamber. The sample is heated to 37.8°C (100°F)

until a constant pressure is observed. This test procedure requires a means to chill the sample, a hot water bath large enough to hold the vapor pressure bomb, and a considerable amount of time to complete. In addition, the technician is required to handle the bomb at several points throughout the test.

Several of the newer test methods for vapor pressure are automated and involve specialized pieces of equipment to conduct the analysis. These automated testers are faster and require less handling by the operator. However, the automated testers still require space and electrical power beyond the capacity of the PQA system.

There has been limited success with attempts to estimate vapor pressure using infrared spectroscopy. It is necessary, however, to conduct further work before infrared could be considered a reliable technique for estimation of vapor pressure. Some combination of infrared spectroscopy and gas chromatography is likely to have more success, although this has yet to be demonstrated in the laboratory.

**Recommendation:** Since vapor pressure is primarily a gasoline test and the test apparatus requirements are beyond the capabilities of the PQA system, it is recommended that a test for vapor pressure not be included in the PQA system.

## 22. Viscosity

Viscosity is a measure of a liquid's resistance to flow. A fuel's viscosity relates to the size of fuel pumps required to provide adequate flow and the configuration and dimensions of injectors to produce proper atomization, thus assuring that full power is available from the engine. The test method to measure fuel viscosity is ASTM D 445, "Standard Test Method for Kinematic Viscosity of Transparent and Opaque Liquids (and the Calculation of Dynamic Viscosity)." For this test, the time is measured for a fixed volume of liquid to flow under gravity through the capillary of a calibrated viscometer under a reproducible driving head and at a closely controlled temperature. Both manual and automated test apparatus are available but require the same equipment. The D 445 procedure requires the use of glass viscometers, an accurately controlled

temperature in a heating bath, and precision timers. The test duration for sample equilibration and analysis is between 6 and 10 minutes. Additionally, the heating bath would require at least 4 to 6 hours to reach the desired test temperature and equilibrate.

Various electromagnetic devices to measure the viscosity of lubricating oils may also be adapted to test fuels. Such instruments include vibrating ball-, wire-, and reed viscometers, and devices that use two electromagnetic coils to drive a piston up and down inside a chamber filled with the test fluid. Piston travel time is related to viscosity. These devices require about 5 mL of sample and results are usually available within 5 minutes.

Preliminary studies indicate that infrared spectroscopy will be able to reliably estimate the viscosity of most diesel and kerosene fuels.

**Recommendation:** The requirements for the performance of the viscosity test are beyond the scope of the PQA system. It is recommended that the PQA system use infrared spectroscopic methods to estimate viscosity.

### 23. Water

Water is one of the most common contaminants in fuels. It can be present as either dissolved or suspended water. Fuels normally contain up to 90 parts per million (ppm) dissolved water. The amount of suspended water in a given fuel varies depending on fuel temperature, fuel composition, and the presence of additives and other contaminants. The presence of water in a fuel system can lead to corrosion, fuel deterioration, and sludge formation, and can promote the growth of microbiological organisms. Water can also freeze in fuel lines and filters and prevent fuel flow to the engine. Dissolved water tends to be of lesser concern than does suspended water, and most often, only the amount of suspended water is measured.

There are essentially two test methods for determination of water content in a fuel. The Karl Fischer titration method (ASTM D 1744) measures for total water, both dissolved and suspended. The centrifuge methods (such as ASTM D 2709, "Standard Test Method for Water and Sediment

in Distillate Fuels by Centrifuge") measure only the suspended water in the fuel. Visual appearance methods also look only for suspended water. The centrifuge method, D 2709, is the method specified in MIL-HDBK-200G.

In D 2709, a 100-mL sample of the fuel is centrifuged for 30 minutes in a centrifuge tube readable to 0.005 volume percent. The space and power requirements for the centrifuge are beyond the scope of the PQA system.

A possible alternative method would be to use an automatic titrator to determine the total water content of the fuel. Some assumption could be made about the amount of dissolved water in the fuel, and the difference would be the amount of suspended water. A titration method could also be used to analyze the fuel before and after the fuel is passed through some type of free water-removing agent. Again, the difference would be the amount of suspended water.

Due to low water concentration dissolved in fuels, preliminary testing with infrared spectroscopy yielded inaccurate results.

**Recommendation:** The test time duration and centrifuge requirements for D 2709 exceed the constraints of the PQA system. Titration methods could be used but would be time-consuming and inaccurate. It is recommended that the visual appearance (clear and bright) method be used as the test method for water (and sediment) in fuels.

#### **24. Water Separation Index, Modified**

The test method for water separation index, modified (WSIM), similar to water reaction and water tolerance, is ASTM D 3948, "Standard Test Method for Determining Water Separation Characteristics of Aviation Turbine Fuels by Portable Separometer." This test method provides a measure of the presence of surfactants in aviation turbine fuels. This test method can detect carryover traces of refinery-treating residues in fuel. It can also detect surface active substances added to or picked up by the fuel during handling from point of production to point of use.



Certain additives can also have an adverse affect on the rating. Some of these substances affect the ability of filter separators to separate free water from the fuel.

In D 3948, a water/fuel sample emulsion is created in a syringe using a high-speed mixer. The emulsion is then expelled from the syringe at a programmed rate through a standard fiber-glass coalescer. The effluent is then analyzed for uncoalesced water by a light transmission measurement. Each test takes 5 to 10 minutes to conduct. The portable separometer that is used for this method is small, easily transportable, and requires little electrical power. No alternative methods for the WSIM test are known.

**Recommendation:** The PQA system should include a portable separometer to measure WSIM.

## **B. Additional Analyses Recommended for Inclusion in the PQA System**

### **1. Aromatic Hydrocarbon Content**

Aromatic hydrocarbon content influences combustion characteristics and indicates the fuel's tendency to smoke, i.e., engines using highly aromatic fuels would give off battlefield "signatures". Aromatic hydrocarbon content also has an effect on fuel stability, cetane number, and possibly lubricity. Two test methods are currently approved for the measurement of aromatic content. These two are ASTM D 1319, "Standard Test Method for Hydrocarbon Types in Liquid Petroleum Products by Fluorescent Indicator Adsorption," and ASTM D 5186, "Standard Test Method for Determination of Aromatic Content of Diesel Fuels by Supercritical Fluid Chromatography."

Test method D 1319 was developed for the analysis of gasolines and is not applicable to diesel fuels. Also, this method requires the use of long, glass, silica-packed columns; a regulated air supply; and an ultraviolet light source. Typical test time is approximately 30 minutes.

Test method D 5186 uses supercritical fluid chromatography to separate the fuel into hydrocarbon types. It is designed for the analysis of diesel fuels and is the method of choice for

determination of aromatics. Cost of the instrument is approximately \$60,000 to \$70,000. The instrument requires a supply of high purity carbon dioxide, a computer system, and specialized software. The typical test time is 15 to 20 minutes. The instrument and associated peripherals would consume approximately \$60,000. The instrument would occupy approximately 20 to 25 cubic feet.

Infrared spectroscopy has been shown to be an excellent estimator of diesel fuel aromatic content. This property could be added to the capabilities of the PQA system by developing an appropriate calibration model for the infrared spectrometer.

**Recommendation:** It is recommended that the PQA system incorporate an infrared spectroscopic method for the analysis of aromatic hydrocarbon content.

## 2. Lubricity

Fuel lubricity is a measure of the ability of a fuel to act as a lubricant for fuel-wetted engine parts. Most of the current test methods for this property use some variation on moving metal components in physical contact and under pressure. None of the currently used test methods could be included in the PQA system in their present configuration. Also, this property can be highly influenced by the presence of additives or contaminants at the ppm level. Consequently, it is not currently feasible to use infrared estimation methods to measure fuel lubricity. The most commonly used test for lubricity at this time is a laboratory wear test called the U.S. Army Scuffing Load Wear Test that uses a modified version of the BOCLE (ASTM D 5001). A redesigned, more rugged test apparatus of reduced size could be developed for inclusion in the PQA system that would allow field testing for fuel lubricity. This would be a pass/fail test based on the specification limits for fuel lubricity. It is recommended that consideration be given to including a test for lubricity in the PQA system.

### **C. Summary of Trade-Off Analysis**

TABLE 3 is a summary of the above trade-off analysis. Each of the fuel properties discussed in this section are listed in the table, along with each of the PQA constraints presented at the beginning of this section. A subjective numerical ranking from 1 to 5 is assigned to each constraint for each fuel property. Please note that the rankings are applied only to the traditional ASTM method of analysis (e.g., for density, the rankings apply to ASTM D 1298). In all cases, a ranking of 5 indicates that the test method for that property meets that particular constraint. A ranking is not given for the constraint to survive chemical and biological attack. In general, an attack with biological weapons should have little effect on any of these test methods; resistance to chemical attack will depend on the nature of the chemical. The majority of these instruments are susceptible to corrosive chemicals.

### **D. Other Properties**

Previous studies have shown that IR will also provide a means to measure oxygenates in fuels and possibly some types of intentional contamination. One limited investigation has shown the potential of FTIR to measure nitrate-based cetane improvers. Each of these analyses, and possibly others, should be considered for inclusion in the PQA.

## **VIII. CONCLUSION**

### **A. Summary of Recommendations**

TABLE 4 presents MIL-HDBK-200G fuel testing requirements and the recommended or usually performed ASTM procedures. The table also notes the existence of commercially available automated or automatic test equipment, alternative test methods, and recommendations for PQA applications. The recommendations are synopses of the recommendations presented in the previous section.

**TABLE 3. PQA Constraints and Rankings for Each Fuel Property\***  
(1 = Worst; 5 = Best)

Property (ASTM method of analysis only)	Constraints							Avg. rank (min. 4.0 required to be in PQA)
	Allows for multiple samples/tests	Self-contained 30 days; 15 samples/day	Be ruggedized	Operate 16 hr/day, min.	Requires only 1 or 2 soldiers to operate	No more than 3-kw generator (battery backup for 1 cycle)	30 min to deploy/begin; 20 min to prepare for departure	Must fit in proposed enclosure
Acid Number	2	2	1	3	4	4	3	4
Accelerated Stability	3	1	1	1	4	1	1	2
Appearance	2	5	5	5	5	5	5	5
Carbon Residue	3	4	3	4	4	1	1	4
Cetane Number	1	1	3	3	4	1	1	1
Cloud, Freeze, & Pour Points	4	4	4	5	5	4	2	4
Color	1	4	4	4	4	4	4	4
Conductivity	4	5	5	4	5	4	5	5
Density/Gravity	2	5	1	4	5	5	4	4
Distillation	1	3	2	4	4	1	2	3
Existent Gum	3	3	4	4	4	1	1	1
Flash Point	4	4	3	4	4	4	4	5
Fuel System Icing Inhibitor	1	2	1	3	3	4	3	4

**TABLE 3. PQA Constraints and Rankings for Each Fuel Property, Cont'd**  
(1 = Worst; 5 = Best)

Property (ASTM method of analysis only)	Constraints							Avg. rank (min. 4.0 required to be in PQA)	
	Allows for multiple samples/tests	Self-contained 30 days; 15 samples/day	Be ruggedized	Operate 16 hr/day, min.	Requires only 1 or 2 soldiers to operate	No more than 3-kw generator (battery backup for 1 cycle)	30 min to deploy/begin; 20 min to prepare for departure		Must fit in proposed enclosure
Knock Value/ Octane No.	1	2	4	3	3	1	1	1	2.0
Lean Mixture/ Rich Mixture	1	2	4	3	3	1	1	1	2.0
Oxidation Stability	2	4	3	4	3	1	1	1	2.4
Sulfur	4	4	4	4	4	4	4	4	4.0
Thermal Stability	2	2	4	4	4	1	1	2	2.5
Vapor Pressure	2	2	4	3	4	1	1	1	2.3
Viscosity	3	4	4	4	4	1	1	2	2.9
Water	3	4	3	4	4	1	4	1	3.0
Water Separation Index	4	3	4	4	4	4	4	5	4.0

\* The rankings are for the specified ASTM procedure.

**TABLE 4. Summary of MIL-HDBK-200G Requirements and Future PQA Recommendations**

Property	Current ASTM D Test Methods	Automated or Automatic Tests Available	Alternative Test Methods	Recommendations for the PQA System	Importance of Property to Proper Operation of Veh (1=Low, 5=High)
Acid Number	974, 3242	Automatic titrator	Not available	Do not include this property in the PQA.	2
Accelerated Stability	2274	No	Not available	The cost and logistical requirements of this test are too great. Do not include this property in the PQA.	1
Appearance	4176	Portable microseparometer	Not available	Include the manual clear and bright test method in the PQA.	3
Carbon Residue	189, 525	Microcarbon residue tester(?)	Not available	This property should be included in the PQA only if it can be estimated by IR. The requirements of the ASTM procedure are beyond the capabilities of the PQA.	2
Cetane Number	613	No	CVCA, IR	Use IR to estimate the cetane number.	5
Cloud Point	2500	Yes	IR	The manual method is not feasible for inclusion in the PQA. The automated testers still require a long test time. IR should be used to estimate this property.	4
Color	2392, 1500, 156	Yes	Not available	Use a visual inspection of the fuel to look for signs of contamination. Color testers are ineffective until their use with dyed fuels is addressed.	1
Conductivity	2624, 3114	Yes, portable	Not available	The PQA should include a portable meter to measure this property.	3

**TABLE 4. Summary of MIL-HDBK-200G Requirements and Future PQA Recommendations, Cont'd**

Property	Current ASTM D Test Methods	Automated or Automatic Tests Available	Alternative Test Methods	Recommendations for the PQA System	Importance of Property to Proper Operation of Veh (1=Low, 5=High)
Corrosion	130	No	Not available	The logistical and power requirements of this test are too large. Do not include this property in the PQA.	2
Density/Gravity	1298	Portable, automated	IR	Use IR method to measure density.	3
Distillation	86	Automated dist.	GC, IR	Use IR techniques to the extent possible. Investigate use of gas chromatography if IR proves insufficient.	4
Existent Gum	381	No	Not available	This property provides little useful information. Hardware requirements are too high. Do not include in the PQA.	2
Filtration Time	5452	D 2068(?);* portable filter blocking app.	Not available	See Particulates.	2
Flash Point	56, 93	Automated	SetaFlash tester (GC/IR?)	The PQA should include a SetaFlash tester used as a pass/fail instrument.	2
Freezing Point	2386	Yes	IR?	See Cloud Point.	4
Fuel System Icing Inhibitor	FTM 5323, 5330, 5340	No	IR	Use IR method to determine FSII concentration.	2
Gum, Unwashed	381	No	Not available	See Existent Gum.	2

TABLE 4. Summary of MIL-HDBK-200G Requirements and Future PQA Recommendations, Cont'd

Property	Current ASTM D Test Methods	Automated or Automatic Tests Available	Alternative Test Methods	Recommendations for the PQA System	Importance of Property to Property Operation of Veh (1=Low, 5=High)
Knock Rating	2699, 2700	No	IR	Use IR method to determine this property.	5
Lead	3341, 2787	XRF, ICP, AA	Not available	Do not include this property in the PQA.	2
Lean Mixture Rating	909	No	Not available	Use IR method if the need for this property remains a requirement. This is an aviation gasoline test.	4
Oxidation Stability	525	No	Not available	Space and power requirements are too high for PQA. This property provides little useful information for immediate use of fuel. Do not include this property in the PQA.	1
Particulates	2276, 5452	D 2068(?)*	Not available	Gravimetric methods are not feasible. Some variation of D 2068 fuel filterability method should be used.	2
Peroxides	3703	No	Not available	Do not include this property in the PQA.	2
Potential Gum	873	No	Not available	The space, time, and power requirements for this test are beyond PQA capacity. Provides little useful data. This test should not be included in the PQA.	1
Pour Point	97	Yes	IR	See Cloud Point.	3



**TABLE 4. Summary of MIL-HDBK-200G Requirements and Future PQA Recommendations, Cont'd**

Property	Current ASTM D Test Methods	Automated or Automatic Tests Available	Alternative Test Methods	Recommendations for the PQA System	Importance of Property to Proper Operation of Veh (1=Low, 5=High)
Rich Mixture Rating	909	No	Not available	See Lean Mixture Rating.	4
Sulfur	1266, 2622	Portable, automated XRF	Not available	Use a portable XRF to measure sulfur.	4
Thermal Stability	3241	No	Not available	Useful test but space, time, and power requirements are too high. This test should not be included in the PQA.	4
Vapor Pressure	323, 2551	Automatic testers	GC(?) GC/IR(?)	Primarily a gasoline requirement. The space, time, and power requirements are beyond the scope of the PQA. Alternate methods show limited success. Recommend this test not be included in the PQA.	4
Viscosity	445, 88	Automated testers	IR	Hardware requirements for this test are too high. Recommend that IR be used for this property.	4
Water Separation Index	2550, 3948	Portable microseparometer	Not available	The PQA should include a portable microseparometer to measure this property.	3
Water Reaction	1094, 3948	Portable microseparometer	Not available	This property is similar to the water separation index. The PQA should use a portable microseparometer for this property.	3
Water Tolerance	4814, 3948	Portable microseparometer	Not available	See Water Reaction.	3

TABLE 4. Summary of MIL-HDBK-200G Requirements and Future PQA Recommendations, Cont'd

Property	Current ASTM D Test Methods	Automated or Automatic Tests Available	Alternative Test Methods	Recommendations for the PQA System	Importance of Property to Proper Operation of Veh (1=Low, 5=High)
Water and Sediment	2709	No	Clear and bright	Use manual clear and bright to detect presence of water and sediment contamination.	3
Water and Solids	2709, 4176	No	Clear and bright	See Water and Sediment.	3

\* Currently in development

Glossary

AA	Atomic Absorption spectroscopy
CVCA	Constant Volume Combustion Apparatus
FSII	Fuel System Icing Inhibitor
FTM	Federal Test Method
GC	Gas Chromatography
ICP	Inductively Coupled Plasma spectroscopy
IR	Infrared spectroscopy
PQA	Petroleum Quality Analysis
XRF	X-ray Fluorescence spectroscopy

Note that TABLE 4 lists more fuel properties than are listed in the trade-off analysis section. Some of the similar or related properties, such as cloud point, freeze point, and pour point, were combined in the trade-off analysis to reduce repetition of like discussions.

TABLE 5 is a summary of the instruments and equipment that are recommended for inclusion in the PQA system. Also included in this table is a list of the fuel properties that the PQA system would be equipped to measure.

**TABLE 5. Test Equipment and Fuel Properties Recommended for Inclusion in the PQA System**

Instrument/Test Equipment	Fuel Properties
Infrared Spec rometer (This will either be an FTIR or NIR, depending on which type is found to best meet the requirements of the PQA.)	Aromatic Hydrocarbon Content Cetane Number Cloud Point Density Distillation Freeze Point Fuel System Icing Inhibitor Knock Value Net Heat of Combustion Octane Number Pour Point Viscosity
X-ray Fluorescence Spectrometer (Tabletop model)	Sulfur Other selected elements, depending on detection limits.
SetaFlash Flash Point Tester	Flash Point
Clear 1-L Bottle or Other Suitable Container (The bottle can be made to fit in the PQA or can be removed for remote testing.)	Clear and Bright Color Visual Appearance
Portable Conductivity Meter	Conductivity
Portable Microseparometer	Water Reaction Water Separation Index Water Tolerance
Fuel Filterability Tester (ASTM D 2068, modified)	Particulates

A typical analysis with the PQA is envisioned as follows:

A fuel sample of approximately one-liter in volume is delivered to the PQA system for analysis. The operator takes the sample container into the PQA enclosure and sets it on the counter. A small siphon tube is placed into the sample. The PQA computer is turned on, and the sample is logged in. The operator signals the computer to begin analysis. A small pump is turned on, and fuel is pumped to the appropriate test equipment. The computer selects test equipment, fuel properties, and pass/fail limits based on the operator's answers to a set of questions. For a complete diesel fuel analysis, the fuel is pumped to an IR test cell (1 to 5 mL), a flash point tester (1 mL), a conductivity test cell (1 to 5 mL), a microseparometer test fluid cell (120 mL), and an X-ray sample cup (10 mL). The pump also delivers approximately 500 mL into a clear bottle. There is a stirrer in the bottle and a natural-light source behind the bottle. The computer turns on the stirrer and the light source, stirs the fuel in the bottle, and signals for the operator to examine the fuel for signs of water and sediment. The fuel in the bottle is then pumped through a test filter to measure particulate content and filterability. The computer records the results of all of the tests with the exception of the visual examination, which is entered by the operator. The expert system in the computer determines the condition of the fuel and rates its usefulness for the desired purpose. The expert system, backed up with a large (CD-ROM) memory, could make recommendations for disposition of off-specification or marginal fuels. The results are automatically transmitted to the operator or designated authority. The operator can also choose to transmit results to the user or relay them verbally. The entire analysis has taken approximately 5 minutes to complete. If a pass/fail test for fuel lubricity is added to the PQA system, the test time and sample required will not change.

## **B. Additional Considerations**

Analytical chemistry requirements to properly evaluate fuels must be continually reassessed in light of new governmental regulations, new engine requirements, and the availability of improved analytical methods and equipment. Although the requirements of the present MIL-HDBK-200G may be kept and adapted to include modern analytical instrumentation, present and future studies

may lead to new scopes of analytical needs as they relate to the needs of the future military commanders.

Most modern analytical instruments contain suitable computer(s) to control the operation and calibration of the instrument and help organize the data into a useful, reportable format. Future computers may (a) integrate data from various instruments and other sources, and (b) convert raw data into information. Such information may be easily compared to computer-based specification requirements. In many instances, the computers may also provide some measure of interpretation and an indication of practical implications of the acquired data.

The combined analytical results may be used to arrive at reasoned conclusions about the sample. These conclusions, with or without the supporting data, may be directly reported to the appropriate military commanders.

Expert systems that not only interpret data of a single instrument but would automatically draw well-reasoned conclusions from results obtained by a battery of analytical methodologies are still to be developed.

Development of "expert systems" requires input from several sources. Input is required from professionals who (a) develop and use these analytical methods and techniques and interpret the results of the various measurements, (b) compile, and where needed, develop additional correlations between laboratory tests and performance, (c) are involved with the development of analytical instrumentation, and (d) are computer experts capable of combining the reasoning of a multitude of experts into a coherent computer program.

## IX. LIST OF ABBREVIATIONS

AA	Atomic Absorption
ASTM	American Society for Testing and Materials
BOCLE	Ball-on-Cylinder Lubricity Evaluator
CVCA	Constant Volume Combustion Apparatus
FSII	Fuel System Icing Inhibitor
FTIR	Fourier Transform Infrared spectroscopy
GC/MS	Gas Chromatography/Mass Spectrometry
ICP	Inductively Coupled Plasma
JFTOT	Jet Fuel Thermal Oxidation Tester
MOS	Military Operations
MTBE	Methyl tertiary-butyl ether
NIR	Near Infrared spectroscopy
NMR	Nuclear Magnetic Resonance spectroscopy
PQA	Petroleum Quality Analysis
RON/MON	Research Octane Number/Motor Octane Number
VCR	Variable Compression Ratio
XRF	X-ray Fluorescence

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## **APPENDIX**

### **The Use of Infrared Spectroscopy to Estimate Fuel Properties**



## The Use of Infrared Spectroscopy to Estimate Fuel Properties

Recent studies at the Belvoir Fuels and Lubricants Research Facility (BFLRF) at Southwest Research Institute (SwRI) (6-8) and at other organizations (9-12) indicate that infrared spectroscopic data may be calibrated to simultaneously, quickly, and objectively determine several pertinent fuel properties, including those of middle distillate fuels (DF-2, JP-5, JP-8, Jet A, and Jet A-1), gasolines, and natural gas.

In a BFLRF/SwRI study to analyze gasoline and middle distillate fuels, the initially selected fuel properties were aromatic hydrocarbon, benzene, and MTBE contents, carbon-to-hydrogen ratio, heat of combustion, cetane number, cetane index, refractive index, viscosity, and density. (Correlations with fuel properties other than those listed are being developed.) Alternately, infrared spectroscopy cannot substitute for elemental analysis to determine, for example, carbon, hydrogen, oxygen, sodium, and vanadium contents.

To illustrate some of the composition-versus-fuel property relationships, the generally accepted arguments listed below may be considered.

- For any given fuel type, high specific gravity is associated with elevated aromatic or naphthenic hydrocarbon concentrations, and low specific gravity with increased paraffinic hydrocarbon contents.
- Heat of combustion of a fuel is influenced by the oxidation state and the related carbon-to-hydrogen ratio of the fuel.
- A fuel will have higher cetane number if the *normal* to *iso*-paraffin ratio is increased.
- Increased aromatic hydrocarbon concentrations decrease cetane number and increase octane number.

- Cloud point of a fuel is decreased by increasing *iso*- to *normal* paraffin ratio and increasing aromatic hydrocarbon content in the fuel.

Thus, these properties are determined by the branching of the saturated hydrocarbons, the ratio of *normal* to *iso*-paraffins, the aromatic hydrocarbon content, including the type and degree of substitution on the aromatic rings, and the ratio of these various constituents. All these chemical features are reflected in the IR spectra of compounds.(13)

For practical considerations, infrared radiation may be subdivided into three general areas: the commonly named near-infrared (near-IR), the midband-infrared (IR), and the far-infrared (far-IR) regions, all defined by their range of frequencies.

Near-infrared occupies the spectral region between the visible and midband infrared segments of the electromagnetic spectrum, i.e., between approximately 800 to 2,000 nanometers (nm), or 0.8 to 2.0 micrometers ( $\mu\text{m}$ ). Midband-infrared is the historically defined "infrared" region. While Fourier transforms are widely used in instrumental analysis, its widespread commercial application to midband infrared spectroscopy to convert the instrument-produced interferograms into useful infrared spectra resulted in the adaptation of the name "Fourier transform infrared" (FTIR) for midband-IR. FTIR spectroscopy normally uses the wavelength region between approximately 2,000 to 50,000 nm (2.0 to 50  $\mu\text{m}$ ), usually between 2.5 to 25  $\mu\text{m}$ . Far-infrared spectral region extends beyond the midband infrared to the microwave region, typically to 1,000- $\mu\text{m}$  wavelength. Since far-IR relates to the geometry and physical structure of molecules rather than to their chemical composition, it is not part of this discussion.

FTIR spectroscopy is based on the measurement of characteristic fundamental resonances associated with a large number of molecular functional groups. In contrast to near-IR, FTIR produces specific, usually sharp, well-defined peaks at substantially increased extinction coefficients. As expected, studies (6, 7) indicated that FTIR spectroscopy provides data in the analysis of middle distillate fuels superior to those derived by near-IR.(8) Properly ruggedized FTIR instrumentation has already been developed for the U.S. Army to withstand takeoff, cruise, and landing in remotely piloted reconnaissance aircraft.

Near-IR spectrum is the result of second and third overtones and combination tones of the fundamental frequencies that produce the directly measurable midband region of the infrared, the FTIR spectrum. In near-IR applications, the use of fiber optics allows a potentially long sample probe to be immersed in the analyte, i.e., the liquid to be analyzed. The signal is then transmitted through the fiber optics to the detector. Since presently available fiber optics have cutoff frequencies at about 11  $\mu\text{m}$  ( $900\text{ cm}^{-1}$  wavenumbers), their application in FTIR is restricted. To analyze hydrocarbon fuels by FTIR, it is advised that the sample be transferred to the spectrometer's sample compartment manually or by a mini-pump through appropriately selected small tubes.

TABLES A-1 and A-2 summarize the various fuel properties that have been estimated from infrared spectra. TABLE A-1 summarizes the currently available correlations derived by FTIR spectroscopy. To illustrate the quality of correlations between the infrared spectrum and fuel properties, the squared correlation coefficients and the standard error of cross validation are also shown. TABLE A-2 presents data obtained from a set of preliminary correlations with near-infrared spectra. Although the near-IR data are preliminary, they do indicate the expected results using this technique.

Results of these studies show that infrared spectroscopy, when combined with multivariate calibration analysis, is a versatile, efficient, and accurate technique for estimating several key fuel properties simultaneously. Overall accuracy of this method is naturally limited by the accuracy of the methods and the laboratory practices that yielded the calibration data used in the statistical analysis. Generally, the accuracy of the FTIR procedure may be compared to the reproducibility of the standard laboratory analysis designed for the direct measurement of specific fuel properties. The excellent correlations among proton nuclear magnetic resonance-, ( $^1\text{H}$ -NMR), ultraviolet- (UV), and mass spectroscopies (MS) and midband infrared spectroscopic results are especially important observations (7) as they substantiate the credibility of the FTIR technique. A good quality infrared spectrum of a fuel may be obtained within approximately 30 seconds to 2 minutes, depending on the instrumentation and spectral region used. From the spectrum, the built-in computer provides simultaneous estimates for those fuel properties for which calibration files exist. Credibility of data, ease and speed of analysis, portability of equipment, the low per-

test cost, and small sample size requirements make the nonintrusive, potentially fully automatic infrared analyses highly desirable in many applications, including those at military base installations and at remote field locations.

**TABLE A-1. Estimation of Fuel Properties by Fourier Transform  
Infrared Spectroscopy**

Fuel Property	Standard Error of Cross Validation	R <sup>2</sup> *
<b>Middle Distillate Fuels</b>		
Heat of combustion, BTU/lb, ASTM D 240	40.5	0.918
Density, g/ml, ASTM D 1298	0.002	0.992
K. vis, cSt, at 40°C, mm <sup>2</sup> /s, ASTM D 445	0.19	0.941
Refractive index at 25°C, ASTM D 1218	0.002	0.996
Lubricity by modified BOCLE, scuff load, g	146	0.989
Cetane number		
ASTM D 613	1.41	0.823
Variable compression ratio (VCR)	6.53	0.885
Constant volume combustion apparatus (CVCA)	3.90	0.958
Cetane index		
ASTM D 976	2.95	0.961
ASTM D 4737	3.80	0.967
Monocyclic aromatic ring carbons, wt%, UV	0.60	0.990
Dicyclic aromatic ring carbons, wt%, UV	0.61	0.985
Total aromatic ring carbons, wt%, UV	1.06	0.990
Saturated hydrocarbons, wt%, ASTM D 2425	4.64	0.955
Aromatic hydrocarbons, wt%		
ASTM D 2425	4.64	0.954
ASTM D 5186	1.08	0.962
Carbon/hydrogen ratio	0.166	0.975
Protons in CH <sub>3</sub> by NMR, %	1.75	0.965
Protons in CH <sub>2</sub> by NMR, %	1.50	0.983
Protons in CH by NMR, %	1.23	0.963
Benzylic protons by NMR, %	1.34	0.984
Aromatic ring protons by NMR, %	0.40	0.997
<b>Gasolines</b>		
Aromatics, vol%, ASTM D 1319	2.02	0.940
Clefin, vol%, ASTM D 1319	1.15	0.951
Saturates, vol%, ASTM D 1319	1.87	0.956
Benzene, vol%, ASTM D 4815, modified	0.089	0.979
MTBE, vol%, ASTM D 4815	0.343	0.985
Total oxygen, wt%	0.119	0.991
RON, ASTM D 2699	0.59	0.943
MON, ASTM D 2700	0.40	0.960
(R+M)/2	0.43	0.959
<b>Natural Gas Samples</b>		
Methane, vol%	1.05	0.995
Ethane, vol%	0.37	0.983
Propane, vol%	0.78	0.985
Carbon/hydrogen ratio	0.021	0.980
Specific gravity	0.010	0.960

\* Squared correlation coefficient

**TABLE A-2. Estimation of Diesel Fuel Properties by Near-Infrared Spectroscopy**

Fuel Property	Root Mean Standard Deviation (Cross Validation)	R <sup>2</sup> *
API, 60°F	0.54	0.97
Density, 60°F	0.0026	0.96
Cloud point, °C	5.08	0.81
Freeze point, °C	5.09	0.83
Viscosity, cSt, at 40°C	0.15	0.90
Distillation temperature		
10%	7.9	0.73
50%	5.6	0.91
90%	12.1	0.71
95%	12.4	0.70
End point	12.4	0.69
Cetane number	2.0	0.63
Hydrogen, %	0.11	0.90
Carbon/hydrogen ratio	0.05	0.93
Heat of combustion		
MJ/kg	0.08	0.81
BTU/lb	32.3	0.81
Aromatics, wt%	1.2	0.96

\* Squared correlation coefficient

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